TESTING DESTRUCTION OF CLAY MINERALS BY SILICA-POOR BRINES IN GALE CRATER, MARS USING LABORATORY AND FIELD EXPERIMENTS. J. E. Valdueza¹, E. M. Hausrath¹, T. F. Bristow², E. B. Rampe³, ¹Department of Geoscience, University of Nevada Las Vegas, Las Vegas, NV (valdueza@unlv.nevada.edu), ²NASA AMES Research Center, CA, ³NASA Johnson Space Center, Houston, TX.

Introduction: The Mars Science Laboratory (MSL) *Curiosity* rover landed in Gale crater to investigate the cause for mineralogical changes seen from orbit, including the clay-sulfate mineral transition observed on its central mound, Aeolis Mons [1]. The lower strata show spectral signatures of clay minerals, hematite, and hydrated Mg sulfates, and the upper strata are dominated by hydrated Mg sulfate signatures [1]. This significant transition has been observed in other locations on Mars [2], and therefore processes related to the clay mineral-sulfate transition are likely important broadly across Mars.

The bulk mineralogy of ~3.7 Ga sedimentary rocks in Gale crater is a product of variations in sediment sources and depositional processes, with overprinting by episodes of early and late diagenetic alteration [3]. Sedimentary analyses of the smectite clay minerals observed in the Glen Torridon (GT) region of Mount Sharp suggest formation in a lacustrine aqueous environment [3]. Examination of the Vera Rubin ridge (VRR) strata indicate that it was formed at the same time as GT and later altered by extensive diagenesis [3]. Recent work suggests that the observed mineral transition from smectites and talc-serpentinites in GT to iron oxides and oxyhydroxides and VRR may have resulted from extensive diagenetic alteration by densitydriven, silica-poor brines sourced from the overlying sulfur-bearing unit on Mount Sharp [5].

This process of alteration by silica-poor brines is observed in limited locations on Earth [6]. We are therefore working to demonstrate the impacts of silica-poor brines on clay mineral alteration in laboratory column and terrestrial analog burial experiments. Column experiments allow the investigation of dissolution and precipitation under conditions that represent a closer analog to natural environments, while burial experiments allow examination of weathering reactions of a known starting material after a specific period of time in a natural field environment. Both methods are valuable for interpreting the water-rock interactions between clay minerals and brines.

In preparation for these longer-term column and burial experiments, we are performing preliminary batch dissolution experiments on materials relevant to Glen Torridon: nontronite and serpentinite. We are using magnesium sulfate brine solutions relevant to those proposed on Mars [2,5]. The results of this study can provide constraints on the characteristics of the diagenetic fluids that formed the altered minerals in

Gale crater. They can also provide insights into the role of brine density-driven diagenesis in past aqueous environments on Mars, which have been proposed to be widespread [5].

Methods:

Preparation of nontronite and serpentinite samples: For these preliminary experiments, nontronite and serpentinite were chosen as starting materials. Nontronites have been detected over widespread areas on the Martian surface [2]. In Gale crater, these nontronite deposits were found to be mixed with Casulfates and Fe³⁺-sulfates, and thus, may have interacted with brines since their formation [7,8]. The presence of serpentine in GT has been observed by [5]. In our next experiments, we will include saponites and talc, both of which are interpreted to be present in Gale crater [5,9].

The nontronite standard NAu-1 [Si_{6.98} Al_{0.95} Fe_{0.07}] [Al_{0.36} Fe_{3.61} Mg_{0.04}]O₂₀(OH)₄ was purchased from the Clay Mineral Society. NAu-1 was mined from the Uley Graphite Mine, Australia, and characterized as predominantly nontronite (>85%), with trace amounts of kaolinite, quartz, and aluminum oxide totaling 10% [10]. Based on previous studies, the NAu-1 nontronite is likely relevant to the bulk clay mineral deposits observed on Mars [7,11]. Before use in the experiments, the NAu-1 was powdered and sieved to <45 μ m-sized aggregates.

The serpentinite was collected as a rock sample from Scorpion Creek in the Klamath Mountains of northern California [12]. The serpentinite was powdered and sieved to obtain the <45 μ m-sized fraction used in the dissolution experiment described below.

Preparation of brine solutions:

A Mg-SO₄ brine was chosen for this work based on [5]. A 2.0 molal (m) concentration of Mg and SO₄ was chosen, based on terrestrial analogs, Basque and Kamloops Lakes in British Columbia and Hot Lake in Washington [13,14,15]. The solutions proposed by [5] are near-neutral, as are the brines of Lake Lewis in Central Australia [6], and Basque, Kamloops, and Hot Lake, that have a near-neutral pH range of 7–8 [13,14,15]. 240.74 g of MgSO₄ (anhydrous) was added to 900 g of 18.2 M Ω deionized water to make a solution with a 2.0 m concentration of Mg and SO₄. The density of the brine solution was 127.04 g/cm³, measured using a volumetric flask. The pH was adjusted to 7.0 using NaOH and H₂SO₄.

Batch dissolution experiment set-up: 180 mL of the 2.0 m MgSO₄ brine solution was added to 0.5 g of nontronite or serpentinite in each 250 ml acid-washed HDPE container. The experiments were performed at 25 °C \pm 0.1 °C in a temperature-controlled shaking water bath. Experimental conditions for each mineral were performed in duplicate with a blank (Figure 1).



Figure 1: Batch dissolution experiment set-up for nontronite and serpentinite. Note that there is one duplicate for each mineral sample and a blank.

Further Work: Further work will include analysis of both the solutions and the reacted minerals. Analysis of the solution chemistry can shed light on dissolution and precipitation reactions, which may also be able to be detected in the solid materials. Solutions will be collected using a pipet, filtered through a 0.2 µm filter, acidified to 2% v/v with HNO3, and then analyzed for Mg, Fe, Al, and Si. Analysis of solid materials will include both samples of the reacted nontronite and serpentinite, as well as precipitates collected on filters during filtration as described above. The mineral assemblage that will precipitate from the solutions will also be modeled, and solutions will be evaporated at different temperatures (e.g., 50 °C, 25 °C, and 0 °C). Analysis of the secondary phases will include XRD, FE-SEM-EDS, TEM, and synchrotron analyses.

We hypothesize that the results of the experiments will include transformation of clay minerals into iron oxides and oxyhydroxides as proposed by [5], releasing silica into solution. As a result, this work will provide important constraints on the diagenetic fluid conditions that formed the observed minerals, leading to a better understanding of the role of brines in the aqueous history on Mars.

Acknowledgements: We would like to acknowledge help from Leena Cycil and the entire Hausrath research group, and funding from the MSL Curiosity Participating Scientist Program.

References: [1] Smith, R.J. et al. (2022) *JGR: Planets, 127*(5). [2] Ehlmann, B.L. and Edwards, C.S. (2014) *Annual Review of Earth and Planetary Sciences, 42*(1), 291–315. [3] Sheppard, R.Y. et al. (2022) *Icarus, 383*(115083). [4] Rampe, E.B. et al. (2020) *JGR: Planets, 125*(9). [5] Bristow, T.F. et al. (2021) *Science, 373*,198–204. [6] English, P.M. (2001) *Sedimentary*

Geology 143(3-4), 219-244. [7] Steiner, M.H. et al. (2016) Geochemica et Cosmochimica Acta, 195, 259–276. [8] Rampe, E.B. et al. (2020) Geochemistry, 80(2). [9] Treiman, A.H. et al. (2014) American Mineralogist, 99(11-12), 2234-2250. [10] Keeling, J.L. et al. (2000) Clays Clay Miner., 48, 537-548. [11] Gainey, S.R. et al. (2014) Geochemica et Cosmochimica Acta, 126, 192-211. [12] Baumeister, J.L. et al. (2015) Applied Geochemistry, 54, 74-84. [13] Nesbitt, H.W. (1990) Fluid-mineral interactions: A tribute to HP Eugster, special publication, 2, 355–371. [14] Renaut, R.W. and Long, P.R. (1989) Sedimentary Geology, 64(4), 239-264. [16] Zachara, J.M et al. (2016) Geochemica et Cosmochimica Acta, 181, 144163. [15] Drever, J.I. (1988) The geochemistry of natural waters, *437*, 333.